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Development of

HIGH-TEMPERATURE, HIGH-CURRENT, ALKALI-METAL, VAPOR-FILLED CERAMIC THYRATRONS AND RECTIFIERS

by

A. W. Coolidge

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-6005

GENERAL ELECTRIC

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Quarterly Progress Report No. 1

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CONTRACT NAS3-6005

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Development of
HIGH-TEMPERATURE, HIGH-CURRENT, ALKALI-METAL VAPOR-FILLED CERAMIC THYRATRONS AND RECTIFIERS

by A. W. Coolidge

General Electric Company

SUMMARY

The purpose of the National Aeronautics and Space Administration Contract NAS3-6005 is to advance the technology and to provide fundamental design data for high-temperature, high-current alkali-metal, vapor-type ceramic tubes. The objectives of this program are to conduct a fundamental investigation of the problem areas associated with high-temperature, vapor-type tubes, and to fabricate and test prototype rectifiers and thyratrons to prove the technology and to provide application data for future reference. Phase I of this program is concerned with the investigation of the fundamental problems and the establishment of the conceptual design of prototype models.

During this report period several General Electric scientists were interviewed on the subject of alkali halides. There was enough diversity of opinion to make it apparent that a test program must be conducted to find answers to the following questions:

1. Will alkali halide dissociate to provide free cesium for tube operation?

2. What are the effects of free halogen in an alkali halide tube?

3. Will free alkalis and halides recombine at the temperature of about 600 degrees centigrade?

4. Will free cesium pressure be adequate to permit cesiated cathode emission?

5. What are the incompatibility problems with alkali halides?

The compatibility of cesium with ceramic-to-metal seal structures was reviewed.

Some rearrangement of thyratron testing and bell-jar exhaust facilities was accomplished. This was done in order to provide two stations capable of testing 15-ampere thyratrons at elevated ambient temperature and in vacuum.

The design of an initial test vehicle for evaluating alkali halides was completed and a cesium-iodide tube was built and tested.

Orders were placed for cesium chloride, cesium iodide, cesium bromide and cesium flouride. Orders were also placed for a few metal filling agents that have vapor pressures in the range of 50 to 500 microns at 600 degrees centigrade.

Some effort was expended on conceptual designs of the 15-ampere thyratron.

Test results on the first cesium-iodide device indicated the possibility of an undesirable halogen cycle occurring within the device.

Analysis of the effects of barium vapor pressure in a tube operating at 600°C indicated that the arrival rate of barium, as a result of its vapor pressure, would be considerably higher than the evaporation rate of barium from a barium-system cathode.

INTRODUCTION

This report describes the work effort during the first quarterly period on National Aeronautics and Space Administration Contract NAS3-6005. The purpose of this contract is to advance the technology and to provide fundamental design data for high-temperature, high-current, alkali-metal, vapor-type ceramic tubes. The objectives of this program are to conduct a fundamental investigation of problem areas associated with high-temperature, vapor-type tubes, and to fabricate and test prototype rectifiers and thyratrons to prove the technology and to provide application for future reference.

As briefly outlined in Article 1 of the contract, the program is divided into two major parts:

PHASE I

Phase I of the program is concerned with the investigation of the fundamental problems and the establishment of the conceptual design of prototype models, that will meet the objective ratings. This program, which will include, literature surveys, paper studies, screening tests and preliminary evaluations, will be concerned with

1. The selection of the alkali-metal vapor and noble-gas mixture which will produce the lowest voltage drop and reduce temperature dependence.

2. A study of the compatibility problems to determine the materials to be used with the selected alkali-metal vapor.

3. A study of ceramic-to-metal seal techniques to determine the materials and the types of seals.

4. An investigation of grid-control techniques for thyratrons.

5. An investigation of the circuit requirements for complete interruption of current while operating from a d-c source.

6. A study of tube-element design and geometry to determine the best combination for minimum size and weight, and for maximum reliability.

7. A study to determine methods of reducing electrical losses.

8. An investigation of mounting methods to determine which are best suited for resisting mechanical shock and for removing heat from the elements.

Following these studies, the investigation will be directed toward producing conceptual designs. The data from this latter investigation will be so presented that it can be utilized for future design work with a minimum of time and effort. The two ceramic thyratron designs developed will have the following specific ratings:

Tube 1 - 300 volts, 15 amperes, 750 volts PIV, 400-2000 cps

Tube 2 - 200 volts, 150 amperes, 750 volts PIV, 400-2000 cps.

PHASE II

Phase II of this program will be concerned with the final design, fabrication and testing of the tubes based on conceptual designs produced in Phase I. Ceramic thyratrons, having ratings of 200 volts, 150 amperes, 750 volts PIV, and 400-2000 cps, will be fabricated and tested in accordance with the contract requirements.

PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES

PUBLICATIONS - None

LECTURES - None

REPORTS

1. Monthly Progress Report No. 1
   Period Covered: June 19 - July 18, 1964
   Author: A. W. Coolidge

2. Monthly Progress Report No. 2
   Period Covered: July 19 - August 18, 1964
   Author: A. W. Coolidge

CONFERENCES

1. Organizations represented:
   - NASA
     - E. A. Koutnik
   - Missile Space Division, General Electric Company
     - R. Edwards
   - Schenectady Tube Operation, General Electric Company
     - E. A. Baum
     - A. W. Coolidge
     - D. L. Schaefer

   Place and Date: General Electric Company, Schenectady, New York, July 13, 1964
   Subject: Review technical progress on this project

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Place and Date: General Electric Company, Schenectady, New York, September 15, 1964

Subject: Review technical progress on this project

TECHNICAL DISCUSSION AND PROGRESS

GENERAL

Vapor control tubes may be used in systems where the minimum rejection temperature may be as high as 600 degrees centigrade, providing the proper attention has been given to the design of the seals and to the problem of suppressing unwanted anode or grid emission. For this type of operation, the high-temperature vapor tube has the following significant potential advantages:

1. low arc drop and consequent low loss

2. freedom from gas clean up.

The most common type of vapor-filled control tube is the mercury thyratron. At room temperature or at relatively low ambient temperatures, the vapor pressure of mercury is appropriate for thyratron operation. (Figure 1)

Cesium has been employed to a lesser extent as the ionizing agent in control tubes. However, because of the relatively lower vapor pressure of cesium (Figure 2), it has been necessary to use these tubes with external heaters to maintain the cesium temperature between 150 and 250 degrees centigrade.

More recently, cesium has been used as the ionizing agent in vapor thermionic converters where optimum operating characteristics are realized when the cesium vapor pressure is about 1.5 millimeters of mercury with a corresponding cesium reservoir temperature of 300 degrees centigrade. In the thermionic converter the presence of cesium greatly enhances cathode emission by means of a process where a monolayer of cesium is deposited on the cathode substrate surface causing a substantial reduction in cathode work function. Cesiated cathode emission densities of 10 to 20 amperes per square centimeter have been readily obtained in the thermionic converter.

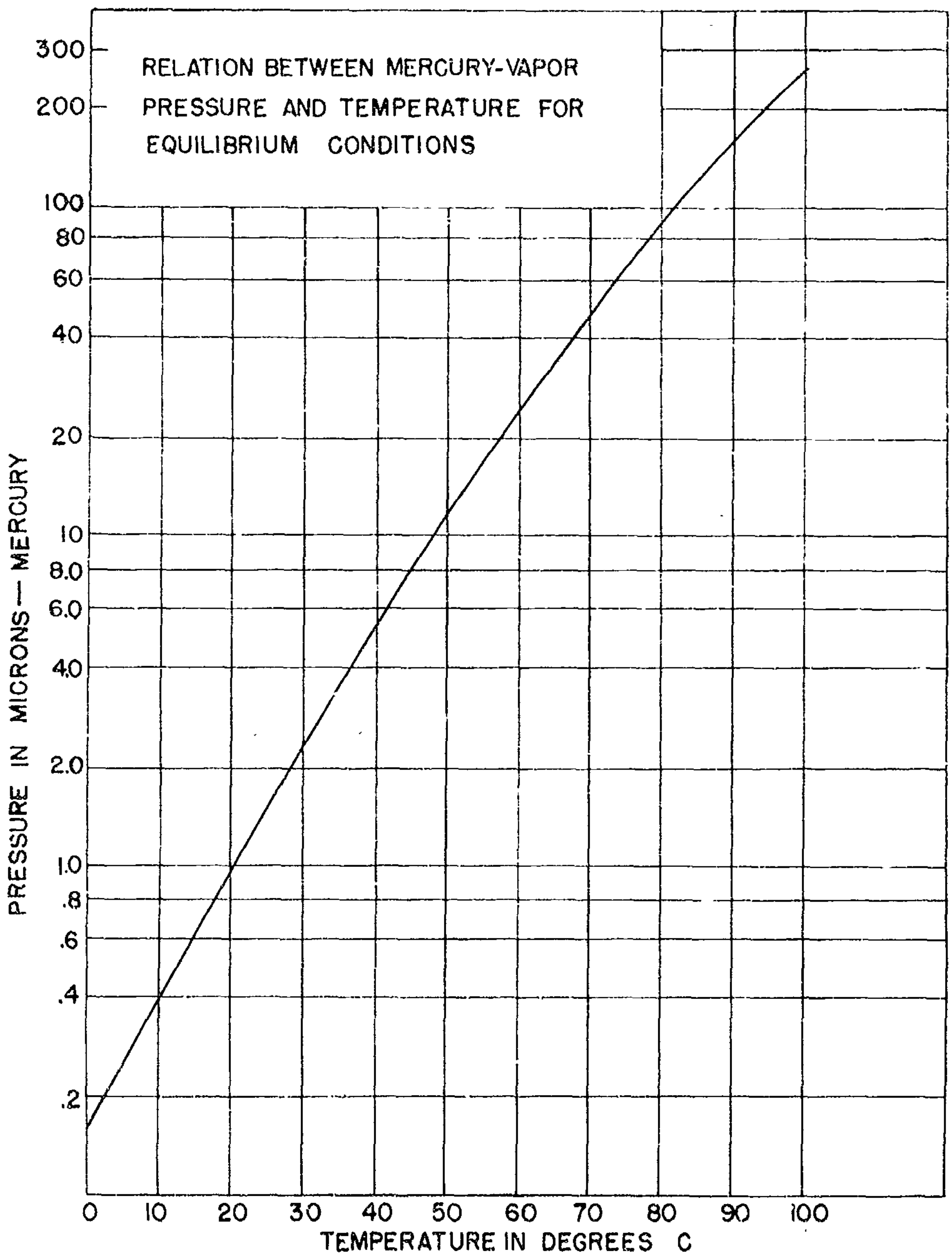

Figure 1 - Relation Between Mercury-Vapor Pressure and Temperature for Equilibrium Conditions

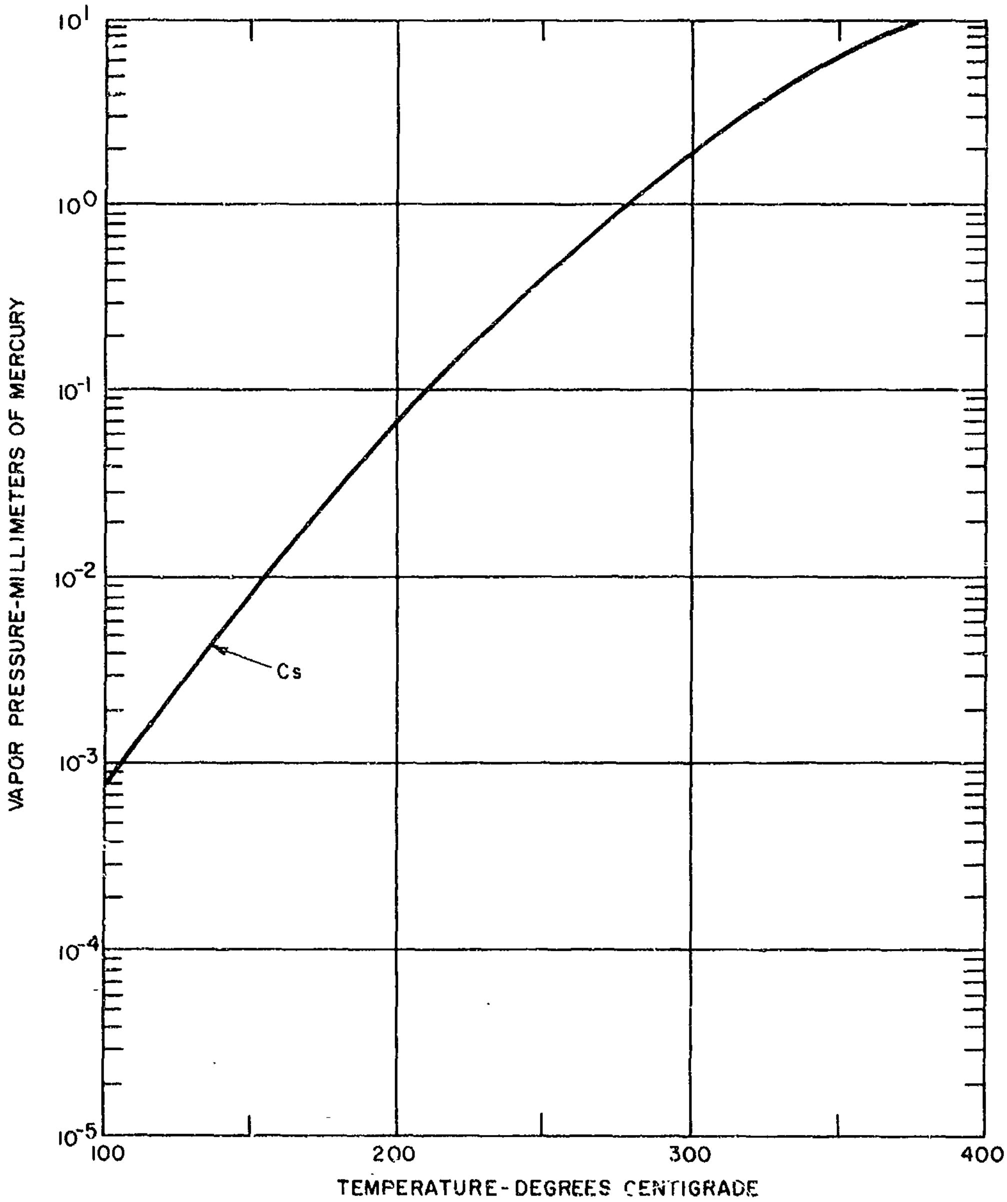

Figure 2 - Relation Between Cesium-Vapor Pressure and Temperature for Equilibrium Conditions

For satisfactory thyratron operation, it is necessary to select a fill material that has a vapor pressure in the range of 50 to 500 microns at 600 degrees centigrade. At 600 degrees centigrade the equilibrium vapor pressures of mercury and cesium are several thousand and several hundred millimeters, respectively. Unquestionably this is high for thyratron tubes. However, thallium and four halides of cesium fall within the fill material range (Figure 3).

Vapor pressure, however, is not the only criteria for satisfactory thyratron operation. In order to minimize the back emission and grid emission currents, the work function of the fill material should be high enough to keep the current levels in the range of 10^{-6} amperes per square centimeter. This necessitates a work function of approximately 3.0 ev. at a temperature of 1150 degrees Kelvin. In order to maintain a low tube loss, the ionization potential should be kept to a minimum. During the next period, it is anticipated that a tube will be fabricated using thallium as the fill material.

It is one of the main objectives of this contract to determine whether an alkali halide such as cesium iodide might be used in a thyratron. Such a tube, it is hoped, would operate as a cesium tube, because of dissociation of the cesium iodide but the vapor pressure would be determined by the vapor pressure curve of the alkali halide.

ENVELOPE

One of the major considerations for envelope design is that all envelope materials must be compatible with the vapor material at elevated temperatures. Considerable background data is available regarding compatibility of envelope materials with cesium, but little information is available regarding their resistance to halogens. Since the objective tube will hopefully function as a cesium tube, it is considered discreet to select envelope materials that are known to have good resistance to attack from cesium. These would include the refractory metals and ceramics having high alumina content, such as Lucalox.*

*General Electric Trademark for high-purity alumina body

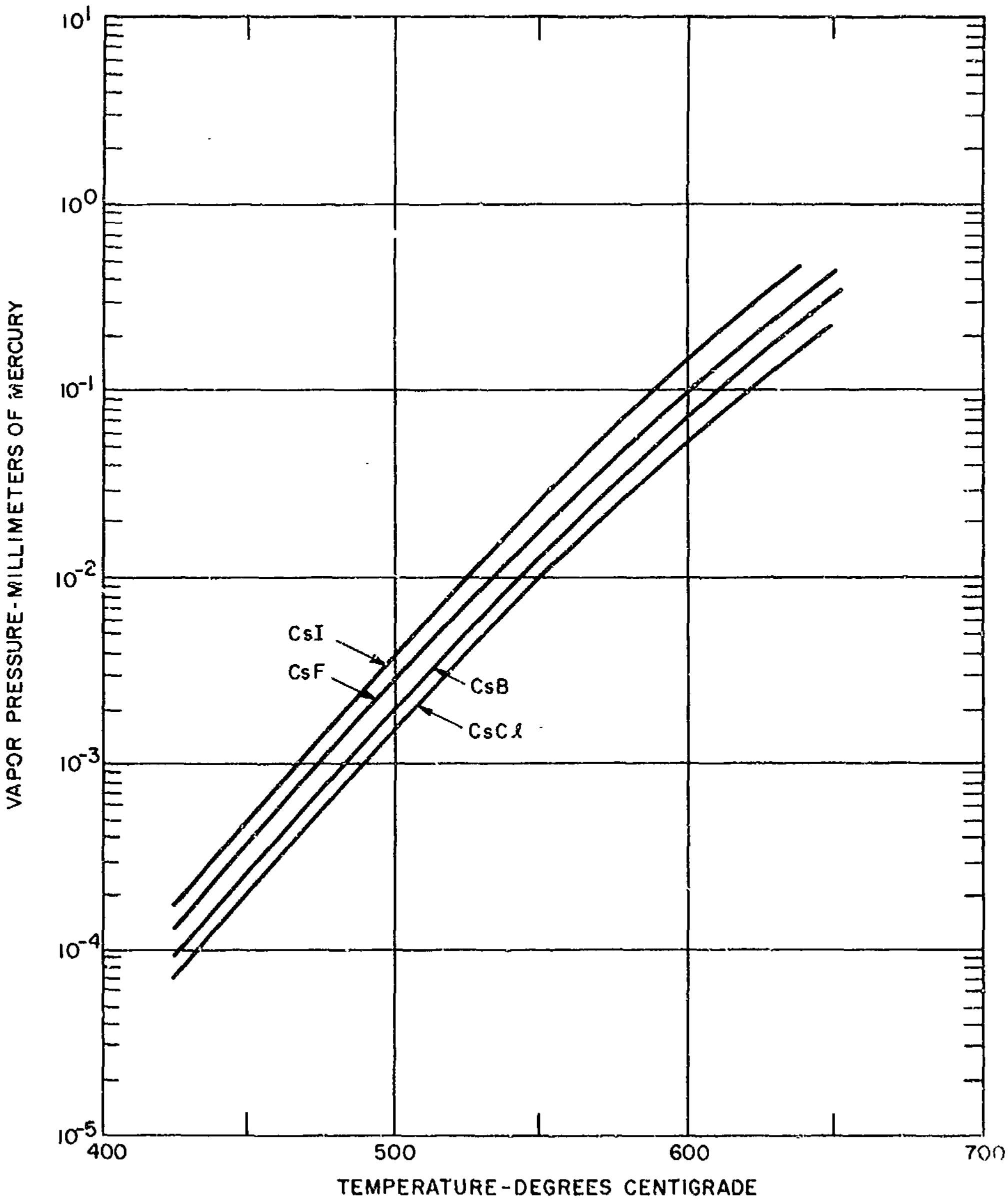

Figure 3 - Relation Between Alkali-Halide-Vapor Pressure and Temperature for Equilibrium Conditions

CATHODE

It is important to determine whether the proper conditions can be obtained in the objective tube for cesium-enhanced cathode emission. Such a cathode would combine simplicity, durability and efficiency. If cesium-enhanced emission does not appear to be a possiblity, other combinations of cathode systems and vapor-fill materials will be needed. In order of descending efficiency, these would include:

1. barium-system cathode with cesium-compound fill
2. barium-system cathode with single-element fill
3. thoriated-tungsten cathode with cesium-compound fill
4. thoriated-tungsten cathode with single-element fill
5. tungsten cathode with cesium-compound fill
6. tungsten cathode with single-element fill.

INITIAL TEST VEHICLE

For the initial test vehicle, a simple diode structure similar to an existing thermionic vapor converter was selected. This structure, shown in Figure 4, consists of a molybdenum emitter (heated by an external oven) and a closely spaced molybdenum anode. To this is attached a tantalum tubulation containing a pellet or reservoir of alkali halide whose temperature is controlled by a second oven. The main body of the tube, which is about as large as a one-inch cube, is placed inside of a third oven. By means of independent oven temperature control, the main structure may be operated in an ambient temperature to 800 degrees centigrade while the emitter temperature may be increased to 1400 degrees centigrade. Because of its remote location, the reservoir temperature may be operated from about 200 to 600 degrees centigrade.

One tube was made with a cesium iodide fill. After exhaust and breakage of the cesium-iodide pellet, the tube ionized when about 340 volts was impressed between anode and cathode. While positive identification of the free gas or vapor in the tube could not be made, it was suspected that there was free iodine present - if so, the equilibrium iodine pressure would be about one Torr at room temperature.

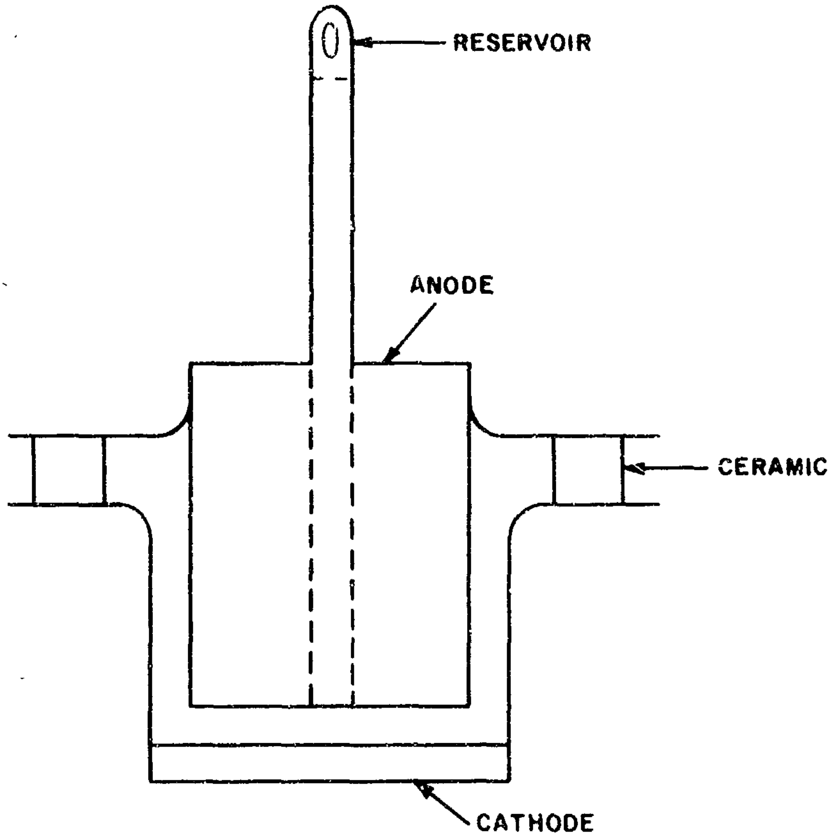

Figure 4 - Schematic of Initial Test Vehicle

As the tube was studied in vacuum environment with the temperature at the anode, the emitter and the reservoir increasing it was apparent that the conduction characteristics in forward and inverse directions were essentially the same. Further, as the temperature was elevated (to a maximum of 615 degrees centigrade ambient, 1000 degrees centigrade at the cathode, 600 degrees centigrade at the anode and 600 degrees centigrade at the reservoir), the tube reacted much like a low-impedance resistor. After the tube was cooled and hi-potted, the tube impedance reached 20 megohms. On another vacuum-environment and high-temperature run, the tube again assumed the characteristics of a low-impedance resistor.

When the tube was opened, a generous metallic coating was evident on the ceramic separating the anode and cathode flanges. X-ray spectroscopic analysis of the coating identified titanium, nickel, cesium and iodine. A titanium-halogen cycle was suspected as the cause of the coating.

In the titanium-halogen cycle, free titanium combines with free iodine to form a titanium-iodide salt which migrates throughout the interior of the tube. Partial dissociation of the salt then occurs, leaving free titanium (displaced from its original location) and free iodine. This cycle may repeat until relocation of free titanium, associated with localized temperature differences within the tube, brings about an equilibrium.

The first tube employed tantalum flange seals, high-purity alumina ceramic, and nickel-titanium brazing washers - a combination known to provide a tube with good cesium resistance. As a result of the apparent halide attack on the structure, the following new approaches will be studied.

Titanium-Nickel Ratio

The first tube was brazed with a combination of brazing washers (containing a surplus of titanium) so that the resulting eutectic melted at 942 degrees centigrade, Figure 5. By essentially reversing the ratio of titanium to nickel, the resulting seal can be affected at 1280 degrees centigrade, so that the resulting braze is primarily $TiNi_3$ plus TiNi as shown near the right-hand side of Figure 5. More important, however, is the fact that there will be less free titanium at the seal structure to trigger a titanium halogen cycle.

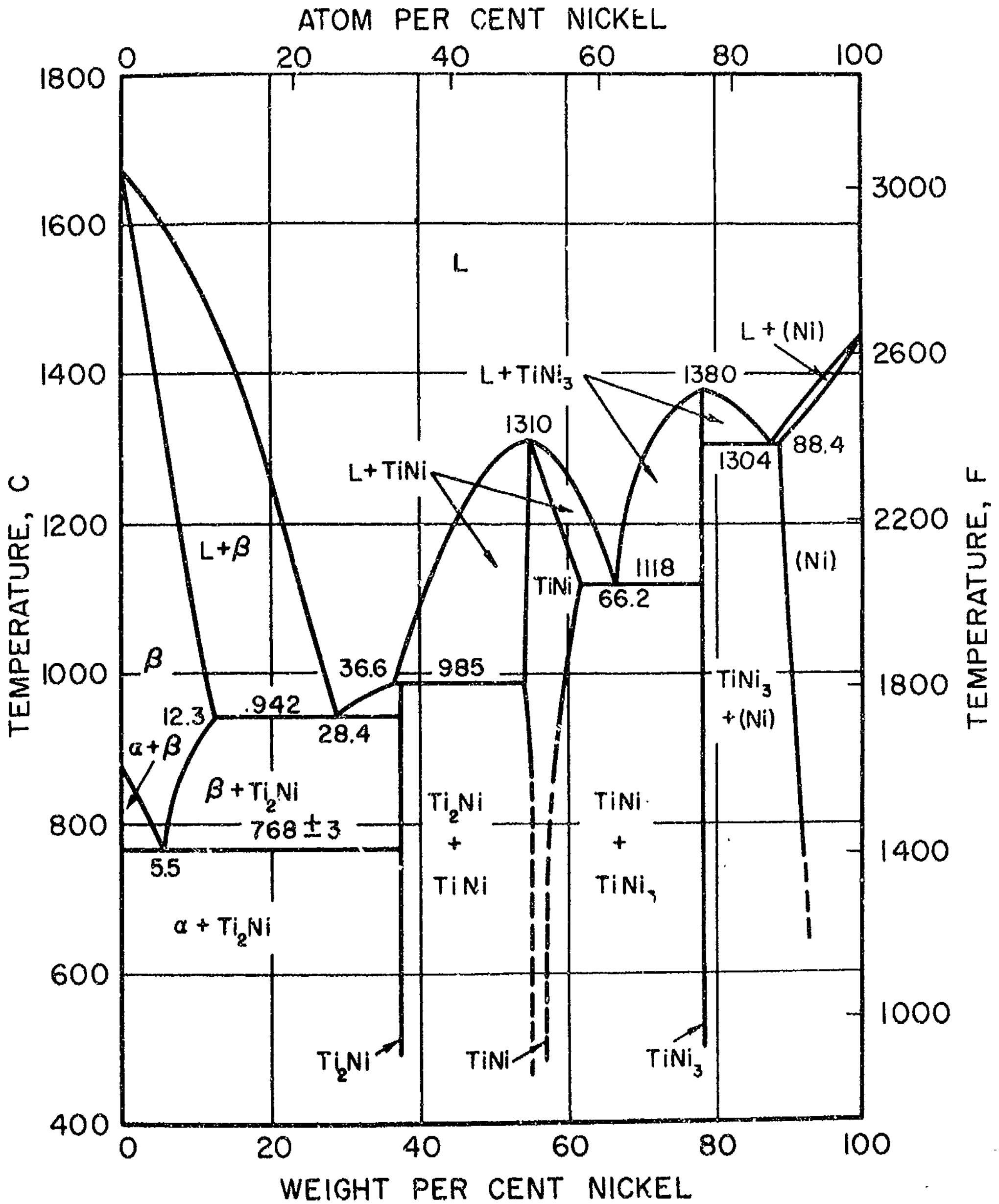

Figure 5 - Nickel Titanium Phase Diagram

Nickel Plate

In this approach, a seal structure will be made with a nickel-rich titanium-nickel eutectic as described in the preceding paragraph. The seal structure will then be nickel plated. This will further reduce the possibility of free titanium being exposed to the halogen.

Palco Brazing

A less commonly used titanium-free brazing system will be evaluated. In this system, the ceramic is metallized with molybdenum and then sealed to the tantalum seals with a compound of palladium and cobalt.

Cesium Tube

A cesium vapor diode is being processed and will be evaluated during the next period. The data obtained will be used as a bench-mark for subsequent alkali-halide tubes. It is expected that the limiting operating temperature will be about 300 to 400 degrees centigrade because of the high cesium vapor pressure. Work by R. K. Steinberg[1] on hot-cathode arcs in cesium vapor reported arc-drops as low as 0.125 volt at currents less than 1 ampere. The limiting effect of a pure cesium vapor device is its inability to hold-off high inverse voltages because of a lowering of the anode work function by partial cesium coverage. However, for low inverse voltages, perhaps to 10 volts, arc drops approaching zero may be obtained by taking advantage of the negative arc-drop characteristics of a close-spaced device.

The cesium tube being readied for test makes use of the thermionic converter structure utilizing a molybdenum cathode and anode. The ceramic-to-metal seal structure is identical to that of the low-temperature (1500 degree centigrade) thermionic converter. Operating times to 3000 hours have been obtained with similar ceramic-to-metal seals at 600 degrees centigrade.[2]

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1. Steinberg, R. K., Hot-Cathode Arcs in Cesium Vapor, Technical Report No. 128, (1949), Research Laboratory of Electronics, M.I.T.
2. Baum, E. A., General Electric Company, Power Tube Department, Evaluation of a Molybdenum Emitter, Low Voltage Arc Thermionic Power Converter, Final Report (ASD-TDR-63-183), Air Force Contract No. AF33(657)-8323.

A hypothetical study was made of the possible effect of high barium-vapor pressure on grid and anode emission - a condition that might arise in a tube (with barium system cathode) if it were immersed in high ambient temperatures.

Industrial thyratrons typically exhibit grid emission currents of less than 10 microamperes. Their barium oxide cathodes typically operate at 800 to 900 degrees centigrade and at this temperature the evaporation rate of barium is in the order of 5×10^{-9} grams per square centimeter per second. Higher grid emission currents can readilly be observed in an industrial thyratron, if the grid is overheated by increasing either the ambient temperature or anode current beyond the tube ratings. By extension, it is assumed that grid emission in a typical industrial thyratron would be substantial, if it were or could be operated in an ambient temperature of 600 degrees centigrade with a barium arrival rate at the grid equal to or greater than 5×10^{-9} grams per square centimeter per second. If this arrival rate (5×10^{-9} grams per square centimeter per second) were considerably larger than that produced by the equilibrium barium vapor pressure, grid emission could be reduced by designing a shielded grid or a series of grids. With this design, the portion of the grid (or grids) exposed to a voltage gradient would receive barium exclusively through the process of arrival as a result of the barium-vapor pressure. Conversely, if the arrival rate (as calculated from the vapor pressure) is considerably greater than 5×10^{-9} grams per square centimeter per second, all portions of the grid would be generously coated with barium regardless of the grid design.

The barium arrival rate is calculated by means of formulas applicable to the kinetic gas laws.[3] The calculations are shown in Appendix 1, and the summarized results are given below.

Condensed Barium Temperature $^{\circ}C$	Barium Arrival Rate ($gm/cm^2/sec$)
200	$1.9\ (10^{-14})$
400	$1.2\ (10^{-7})$
600	$8.7\ (10^{-5})$
800	$3.9\ (10^{-3})$
1000	$6.0\ (10^{-2})$

3. Cobine, J. D., Gaseous Conductors, McGraw-Hill Book Company, Inc., New York, 1941.

Recapitulating, in the above hypothetical example, the evaporation rate from the cathode is 5×10^{-9} grams per square centimeter per second whereas the arrival rate, because of the barium vapor pressure (at 600 degrees centigrade) is 8.7×10^{-5} grams per square centimeter per second. Since the latter rate is some t. n thousand times higher than the evaporation rate, there is little hope of reducing grid emission by means of baffling. Some reduction might be realized by heating the grid so as to reduce the net amount of barium at the grid. Also, a high work function material such as graphite could be employed for minimum grid emission.

PROGRAM FOR NEXT REPORT PERIOD

During the next report period, additional test diodes will be constructed. ' ese diodes will have the following special features:

1. Pure cesium fill.

2. Brazing compound to be high in nickel and low in titanium content.

3. Same as (2) above, except inside of tube will be nickel plated.

4. Ceramics will be metallized with molybdenum and brazed with a compound of palladium and cobalt.

Test data will be obtained to indicate potential capabilities and limitations regarding cathode emission and spurious anode and grid emission.

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APPENDIX I
DERIVATION OF BARIUM ARRIVAL RATE

The arrival rate of barium at a surface as a result of the equilibrium barium vapor pressure existing at different temperatures can be determined by the following:

(1) $$n_r = \frac{n\bar{c}}{4}$$

where n_r = number of particles arriving at an area of 1 cm^2 in 1 sec

n = number of particles per centimeter cube

$\bar{c}$ = average velocity of particles, cm/sec

(2) $$n = \frac{b\,P\,273}{760\,T}$$

where $b = 27.05 \times 10^{18}$ molecules/cc at N.T.P.

P = vapor pressure of barium in millimeters of mercury

T = condensed barium temperature in degrees Kelvin

(3) $$\bar{c} = 1.868\,(10^{-8})\sqrt{\frac{T}{m}}$$

where m = mass of a barium atom, grams

(4) $$n_r = \frac{b\,(P)\,273\,(1.868)\,(10^{-8})}{760\,(T)\,\sqrt{m}\,4}\sqrt{T}$$

$$= \frac{0.47\,(10^{22})\,P}{\sqrt{T}}$$

(5) $$N_B = \frac{1}{W_H\,N_A}$$

where N_B = number of barium atoms in a gram

W_H = weight of hydrogen atom, grams

N_A = atomic weight of barium

$$\therefore \quad N_B = \frac{1}{1.6617\,(10^{-24})\,56} = 1.1\,(10^{22})$$

$$W_a = \frac{n_r}{1.1\,(10^{22})}$$

where W_a = barium arrival weight in terms of grams/cm^2/sec.

Arrival Rates of Barium as a Function of Temperature

T^oC	T^oK	P	$\sqrt{T}$	n_r	W_a
0	273		17	17	
200	473	$1\,(10^{-12})$	22	$2.1\,(10^{8})$	$1.9\,(10^{-14})$
400	673	$7\,(10^{-6})$	26	$1.3\,(10^{15})$	$1.2\,(10^{-7})$
600	873	$6\,(10^{-3})$	30	$9.4\,(10^{17})$	$8.7\,(10^{-5})$
800	1073	$3\,(10^{-1})$	33	$4.2\,(10^{19})$	$3.9\,(10^{-3})$
1000	1273	5	36	$6.5\,(10^{20})$	$6.0\,(10^{-2})$

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ABSTRACT

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A test vehicle was designed for the initial evaluation of alkali-halide filling agents that might be used in vapor discharge tubes designed to operate at 600°C ambient temperature. Test results from the first device indicated the possibility of an undesirable halogen cycle occurring within the device. Proposed countermeasures are discussed. Author